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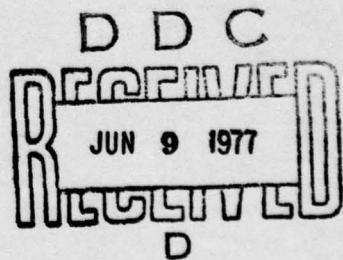NATIONAL BUREAU OF STANDARDS-1963-A

RADC-TR-77-16
Interim Technical Report
January 1977

ANALYSIS OF SEMICONDUCTOR STRUCTURES BY

NUCLEAR AND ELECTRICAL TECHNIQUES

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JUN 9 1977

Dr. James W. Mayer is the responsible investigator for this contract. D. Eirug Davies (ETSD), is the RADC Project Engineer.

This report has been reviewed by the RADC Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

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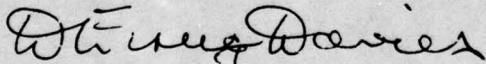
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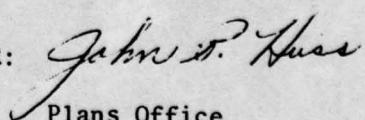# REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
RADC-TR-77-16		

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
Analysis of Semiconductor Structures by Nuclear and Electrical Techniques	Interim Technical Report.
	6. PERFORMING ORG. REPORT NUMBER
	Scientific Report No. 4

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
Joseph M. Harris, Marc-A. Nicolet, Silvanus S. Lau, Johnson O. Olowolafe, James W. Mayer	F19628-75-C-0008

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
California Institute of Technology Electrical Engineering Department Pasadena, California 91125	61102F 2305J101 J1

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Deputy for Electronic Technology (RADC/ETSD) Hanscom AFB, MA. 01731 Monitor: D. Eirug Davies	January 1977
	13. NUMBER OF PAGES
	52

14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)	15. SECURITY CLASS. (of this report)
Same	UNCLASSIFIED
54p.	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Distribution unlimited; approved for public release.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Metallization of Silicon
Reaction of Sputtered Ti-W films with Si
Reaction of evaporated Cr films with Si or Pd_2Si on Si
Cr Films Barriers to Al reaction with Pd_2Si

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report contains three experimental studies which are all closely related to problems of Si metallization.

Thin films consisting of a uniform mixture of Ti and W are often used in contact pads as barriers to prevent the Au of the metal strip from touching the Si to be contacted. We have investigated Ti-W films of an atomic composition ratio Ti:W = 0.3:0.7 sputter-deposited on Si substrates by MeV ^{4}He backscattering spectrometry, x-ray diffraction and secondary electron microscopy

as a function of time during anneals at about 700°C in vacuum. The films react with the substrate and form a ternary silicide $Ti_xW_{1-x}Si_2$ at a linear rate of the order of 1/2 Å/sec (at 725°C). The rate is thermally activated and has an activation energy of 4.5 eV. The rate also depends on the substrate orientation; <111> is slowest, <110> intermediate, and 100 fastest. The dc bias applied during sputter-deposition also influences the rate.

Thin vacuum-evaporated films of Cr react with a Si substrate at about 400°C in vacuum and form $CrSi_2$. The growth rate of the silicide layer is linear in time with an activation energy of 1.7 ± 0.1 eV and a value of 0.7 Å/sec at 450°C. The rate is the same for <111>- and <100>-oriented substrates. For long anneal times, the rate becomes sublinear, an effect attributed to a contaminant, probably oxygen. On Si wafers covered with a Pd_2Si film, Cr also forms $CrSi_2$; the layer of Pd_2Si underneath retains its integrity during the reaction. The growth rate of $CrSi_2$ on Pd_2Si is independent of the thickness of the Pd_2Si layer, and has a similar value and activation energy as for the $CrSi_2$ growth on Si.

Thin films of Al in contact with Pd_2Si layers on Si induce non-uniform erosion of the silicide when heated between 300 and 450°C. When a thin film of Cr is interposed between the Pd_2Si and the Al, intermixing of Pd_2Si and Al is suppressed up to 500°C and 2 hrs. On the Pd_2Si side, $CrSi_2$ forms; on the Al side, $CrAl_x$ forms. As long as unreacted Cr remains, separation between Al and Pd_2Si is maintained ("reactive barrier" concept).

TABLE OF CONTENTS

ABSTRACT

MeV backscattering spectrometry and x-ray diffract-tion are used to investigate the behavior of sputter-deposited Ti-W mixed films on Si substrates. During vacuum anneals at temperatures of 700°C for several hours, the metallization layer reacts with the substrate. Backscattering analysis shows that the resulting compound layer is uniform in composition and contains Ti, W and Si. The Ti:W ratio in the compound corresponds to that of the deposited metal film. X-ray ana-lyses with Read and Guinier cameras reveal the presence of the ternary $Ti_{(x)}W_{(1-x)}Si_2$ compound. Its composition is unaffected by oxygen contamination during anneal, but the reaction rate is affected. The rate measured on samples with about 15% oxygen contamination is linear, of theorder of 0.5 Å/sec at 725°C, and depends on the crystallographic orientation of the substrate and the d-c bias during sputter deposition of the Ti-W film.

We have measured the kinetic rate of formation of $CrSi_2$ using 2.0 MeV $^4He^+$ backscattering spectrometry. $CrSi_2$ was formed on single crystal <100>- and <111>-oriented Si and on Pd_2Si grown on <100> Si. For both Si-Cr and Si-Pd_2Si-Cr samples the rate of growth of $CrSi_2$ is linear in time with an activation energy of 1.7 ± 0.1 eV, and a value of 0.7 Å/sec at 450°C. For all annealing temperatures, the growth becomes non-linear at long annealing times. The non-linearity is attributed to a contaminant, probably oxygen. On Pd_2Si, $CrSi_2$ starts to

form at about 400°C, while on Si, $CrSi_2$ formation is observed at 450°C and above. The difference in formation temperatures is due to contamination at the Si-Cr interface, quite probably a thin oxide layer. The growth rate of $CrSi_2$ in the $Si-Pd_2Si-Cr$ samples is independent of the thickness of Pd_2Si.

Backscattering spectrometry with 2.3 and 2.0 MeV $^4He^+$ have been used to study the role of Cr as a barrier in the interaction of Pd_2Si with Al. Samples of palladium silicide (Pd_2Si) grown on Si <100> single crystal and Al evaporated on top, in that order, showed a substantial intermixture of Pd_2Si and Al, and a non-uniform erosion of the Pd_2Si-Si interface when heated between 300 and 450°C. With a thin layer of Cr (300 to 1500Å) interposed between Pd and Al intermixing of Pd_2Si and Al was suppressed for temperatures up to 500°C and times up to 2 hours. In these samples distinct sublayers of Pd_2Si, $CrSi_2$ and $CrAl_x$ (where the values of x depends on the relative thicknesses of Al and Cr) are formed. We have noted that whenever there is a thin unreached Cr layer the spectra of the distinct sublayers show sharp boundaries.

A. Introduction

This report contains three experimental studies which are all closely related to practical problems.

The first investigation was submitted to us by the Jet Propulsion Laboratory. For the high reliability needed in space missions, the Ti-W metallization used in the contact pads of certain semiconductor devices seemed questionable. Not much later, the R & D Laboratory of Fairchild Semiconductors in Palo Alto approached us with the same request to look into the metallurgical processes of this contacting method. Section B of this report summarizes the results of our investigations. In its industrial application, this contact is covered by a layer of Au, which was omitted in our work. Preliminary studies performed with such a Au layer on top of the ternary $Ti_xW_{1-x}Si_2$ layer showed catastrophic failures at temperatures of about 350°C, which is below the Si-Au eutectic temperature of 370°. The failure is probably related to the large stresses contained in the ternary silicide layer. It would be most desirable to continue this investigation.

Sections C and D form a pair of companion investigations. There is much interest in Pd_2Si as a possible substitute for Pt_2Si to contact Si, but it is well known that Pd_2Si layer can desintegrate under the attack of Al layers deposited on top of them. In Section C, we show that an additional silicide layer of $CrSi_2$ can be formed on top of

an existing Pd_2Si layer without affecting the integrity of the Pd_2Si layer and its interface against the Si substrate. We then show in section D that if a Cr layer of sufficient thickness is placed on top of a Pd_2Si layer before the Al is deposited, the Cr will effectively act as a barrier between the Al and Pd_2Si. During annealing, the Cr film will react at both its interfaces, forming $CrSi_2$ towards the Pd_2Si side, and $CrAl_x$ towards the Al side; but as long as some elemental Cr is left unconsumed, the separation between the Al and the Pd_2Si is effectively maintained.

We believe that a separation between two incompatible metal layers can be more effectively and more predictably established with such a reacting barrier than with so-called "diffusion barriers." On close scrutiny, most diffusion barriers turn out to be poor barriers, or to be no barriers at all. The concept of a reacting barrier has not yet gained general acceptance in the semiconductor industry, but we feel that its introduction will become widespread when its merits are pulicized by studies such as those given in this report.

B. STUDIES OF THE Ti-W METALLIZATION SYSTEM ON Si*

I. Introduction

Titanium and tungsten have both been used for many years as materials for metallizing integrated circuits.[1] Tungsten is used because its coefficient of expansion closely matches that of silicon, and titanium is used because of its strong adherence to oxides. A metallization scheme has also been developed which uses a mixture of titanium and tungsten.[2] Like many of the transition materials, Ti and W both form silicides. The formation of WSi_2 from thin tungsten films on Si has been studied by several authors.[3,4] The formation of $TiSi_2$ by thin films on Si has also been studied,[5] thought not to as great an extent as WSi_2. To our knowledge, the present investigation is the first to consider the interaction of a mixed thin film with silicon. This study shows that, like Ti and W individually, a thin composite layer of Ti and W deposited on Si by sputtering and annealed in vacuum form a ternary disilicide.

II. Sample Preparation

Films of 1000-1500Å were deposited by RF sputtering from an arc-melted $Ti_{0.3}W_{0.7}$ target onto silicon substrates.

The silicon substrates were n- or p-type, 1-10 ohm-cm single crystal wafers of <111>, <110> or <100> orientations which had been mechanically polished and chemically etched.

During deposition, the substrates rested on a water-cooled pallet and the deposition temperature was monitored by a shielded iron-constantan thermocouple placed on the substrate surface. Substrates were loaded through a side loader which was evacuated by a cryogenic pumping station so as to prevent contamination of the target during loading.

Prior to loading the silicon substrates were dipped in HF, rinsed in deionized water, and dried with high purity isopropanol. After loading the sputtering chamber was evacuated to a background pressure of 1×10^{-6} Torr. Argon of 5N purity which had passed through a titanium purifier was used to backfill the chamber. The Ti-W target was given a short presputter to insure a clean surface, and the substrates were sputter-cleaned immediately before deposition.

Anneals were performed in an evacuated quartz-tube furnace. The furnace was pumped from one end by a LN_2 trapped oil diffusion pump and from the other end by a water-cooled titanium sublimation pump. The vacuum during anneals was typically 7×10^{-7} Torr. The temperature in the center of the furnace was measured by a Chromel-Alumel thermocouple which had been calibrated to an accuracy of $\pm 1°C$ against a mercury thermometer to a temperature of 350°C. The thermometer was calibrated against the freezing point and the boiling point (corrected for barometric pressure) of H_2O. The temp-

erature stability of the furnace was measured to be ± 2°C over a period of 20 hr. The furnace was constructed so that many samples could be loaded and annealed sequentially during a single pump-down, and samples were always placed at the position within the furnace where it had been calibrated. Samples could be grouped and annealed simultaneously in the furnace.

III. Results

Characterization of ternary silicide. Films of Ti-W having about 30 a/o Ti (10% by weight) prepared as described above were vacuum annealed at 800°C for 20 min. The surface changed from the smooth metallic luster of Ti-W to a deep silver-gray. Examination by SEM at 4500x magnification revealed a uniform and gently undulating surface. The undulations were typically 2.5 μm across and < 0.05 μm in height (as determined by measurement with a Sloan Dektak).

X-ray diffraction analysis by Reed camera revealed the presence of only one compound. The diffraction pattern corresponds to that described by the ASTM powder diffraction compliation No. 6-0599. This compound has a chemical formula of $Ti_xW_ySi_2$, where $x + y = 1$, with a hexagonal $CrSi_2$-type (C-40) structure. X-ray analysis by the Guinier camera supported the Reed camera results in that no crystal structures other than the C-40 type were detectable. The line spacings from the Guinier photographs gave cell parameters of a_o = 4.61 ± 0.01Å and c_o = 6.48 ± 0.01Å.

2 MeV ^{4}He$^+$ BS analysis of films reacted at 725°C for 40 min revealed that the atomic concentration ratio of the films is Ti:W:Si = 0.3:0.7:2.0 (Fig. 1). The compound maintains this composition at temperatures ranging from 675° to 900°C. Additional experiments established that the compound formed was independent of substrate orientation, doping type, substrate bias during sputter deposition, and the sample contamination by oxygen during annealing.

Once formed, the compound adheres strongly to the silicon substrate. The compound seems unaffected by hot H_2O_2, HF or CP-4, and dissolves only slowly in aqua regia. Indium solder would not adhere to the compound.

Kinetics of silicide formation. The reaction rate of the compound formation was investigated by BS on samples annealed in vacuum for increasing periods of time. To translate the energy scale of a BS spectrum into a depth scale, we assumed a density of 7.54 x 10^{22} atom/cm^3 for the compound, as calculated from the measured unit cell parameters. Using this density, 10 keV in a BS spectrum corresponds to about 106Å of compound.

Reaction rate studies at 750°, 725° and 700°C were performed on covered samples annealed at 7 x 10^{-7} Torr. Samples annealed at each temperature were all cut from the same wafer and loaded simultaneously. The samples were then annealed sequentially. When precautions to reproduce the vacuum were taken, the results were reproducible. The analysis of the backscattering yields established that after anneal all

the samples were contaminated 15-20%, presumably by oxygen.
The reaction has linear time dependence at all temperatures
and over the entire range of oxygen contamination. An ap-
parent activation energy of 4.5 eV is determined from the
reaction rate vs. temperature (Fig. 2).

The rate of reaction is influenced by several para-
meters. This fact was established by comparing two samples
which differed only in the parameter of interest. These
sample pairs were sandwiched together with the metallized
sides face to face and annealed in a vacuum similar to that
used in the rate vs. temperature studies. This procedure
also gave reproducible results. From such comparison, it was
established that samples deposited on <111> silicon sub-
strates react slower than those deposited on <110>, and
samples prepared on <100> react the fastest. On the other
hand, the dopant type of the Si substrate had no measurable
effect on the reaction rate, nor did changes of the doping
level from 2 to 10 ohm-cm.

IV. Discussion and Conclusion

Transition metal silicides typically form complete
solid solutions when the two constituting binary silicides
are isomorphic. A partial solid solution or ternary compound
forms when the two binary silicides are noniosmorphic.[6]
$TiSi_2$ has an orthorhombic (C-54) structure with a packing
sequence ABCD, but SWi_2 has a tetragonal (C-11b) structure
with a packing sequence ABAB. Hence one expects that a ternary

compound will form with Ti, W and Si. Formation of ternary compounds has also been reported in both the Ti-Mo-Si system and the Ti-Re-Si system.[6]

The Ti-W-Si system has been studied by Nowotny.[7] He reports a ternary disilicide of composition $Ti_xW_{1-x}Si_2$ for $x > 0.6$ but a mixture of $TiSi_2$ and WSi_2 for $x < 0.6$. In the present case, $x = 0.3$; compound formation is observed nevertheless. This discrepancy between Nowotny and the present work could possibly be due to the fact that Nowotny investigated bulk samples prepared by high pressure sintering at 1300°C while we consider thin-film samples prepared near 750°C.

We attribute the surface distortion after compound formation to the volume expansion the film experiences as a result of Si inclusion. This expansion is substantial since the film undergoes only a small atomic density change (approximately 6.14×10^{22} atom/cm^2 for the initial Ti-W layer, as calculated from the weighted sum of the elemental densities; approximately 7.54×10^{22} atom/cm^3 for $Ti_{0.3}W_{0.7}Si_2$ calculated for the compound from the x-ray data).

A reduction of reaction rates by oxygen contamination has been observed by Kräutle[8] in the formation of VSi_2 by thin films of V on Si. It is remarkable that the rate of reaction is closely linear in spite of considerably oxygen contamination. The observations that the rate remains linear at reduced oxygen contamination and that the substrate crystal orientation also influences the rate, is consistent with a reaction-limited mechanism. This hypothesis is further sup-

ported by the fact that Borders[4] reports linear rates for the WSi_2 formation. No published data exist for reaction rates of Ti films on Si substrates.

The observed activation energy of 4.5 eV is high. Sinha[9] also reported a high activation energy of 4.4 eV for WSi_2 growing at the expense of PtSi. On the other hand, the activation energies quoted for the formation of WSi_2 films on Si range from 2 to 3 eV.[4] Our value for 4.5 eV may thus be the result of $Ti_{0.3}W_{0.7}Si_2$ growing at the expense of an oxide of titanium and/or tungsten. An argument against this hypothesis is the fact that no oxides of Ti or W were detected in the x-ray photographs. The x-ray analysis, however, is not very sensitive to small oxide concentrations over narrow regions such as the reaction interface. At present, the high value of the activation energy is not understood.

Since we were unable to perform anneals without introducing detectable amounts of contamination, the kinetics data presented here are to be considered preliminary. It would also be worthwhile to extend this study to Ti-W films with various initial compositions, or to other disilicide-forming bimetal combinations. The results would be of value to the subject of ternary silicides in general, and to their possible application in silicon device technology in particular.

V.   References

*   Work supported in part by the Air Force Cambridge Research Laboratories (D.E. Davies) and the Jet Propulsion Laboratory (J. Maserjian and J. Boreham).

1. J.L. Vossen, J. Vacuum Sci. Technol. 11, 60 (1974).

2. J.A. Cunningham, IEEE Trans. on Reliability R19, 182 (1970).

3. L.D. Locker and C.D. Capio, J. Appl. Phys. 44, 4366 (1973); A.K. Sinha, M.H. Reed and T.E. Smith, J. Electro-chem. Soc. 120, 1775 (1973).

4. J.A. Borders and J.N. Sweet, in the Proceedings of the Intl. Conf. on Applications of Ion Beams to Metals, Eds. S.T. Picraux, E.P EerNisse and F.L. Vook (Plenum Press, New York, 1974) p. 179.

5. H. Kräutle, M-A. Nicolet and J.W. Mayer, ibid., p. 193. See also, Phys. Status Solidi a10, k33 (1973).

6. H.J. Goldschmidt, Interstitial Alloys, Plenum Press, New York, 1967, p. 323.

7. H. Nowotny, R. Kieffer and H. Schachner, M.L. Chem. 83, 1243 (1952).

8. H. Kräutle, M-A. Nicolet and J.W. Mayer, J. Appl. Phys. 45, 3304 (1974).

9. A.K. Sinha and T.E. Smith, ibid., 44, 3465 (1973).

VI. Figure Captions

Figure 1. Backscattering spectra showing a virgin (room
temperature) and a covered, annealed (725°C, 40
min, 7 x 10^{-7} Torr) sample of Ti-W on Si. The
Si substrate is <111> single crystal n-type with
resistivity of 10 ohm-cm. Arrows indicated the
position of signals from Si, Ti and W on the
sample surface.

Figure 2. (Left) Plot of compound thickness (expressed in
terms of backscattering energy loss for 2.0 MeV
$^4He^+$ ions, 10 keV corresponds to about 106Å of
compound) vs. anneal time, t, minus warm-up time
t_o. (Right) Plot of log of reaction rate vs. re-
ciprocal anneal temperature (yields activation
energy of 4.5 eV).

BACKSCATTERING SPECTRA SHOWING
REACTION OF Ti-W WITH Si

T.3 W.7 Si2 -50V BIAS
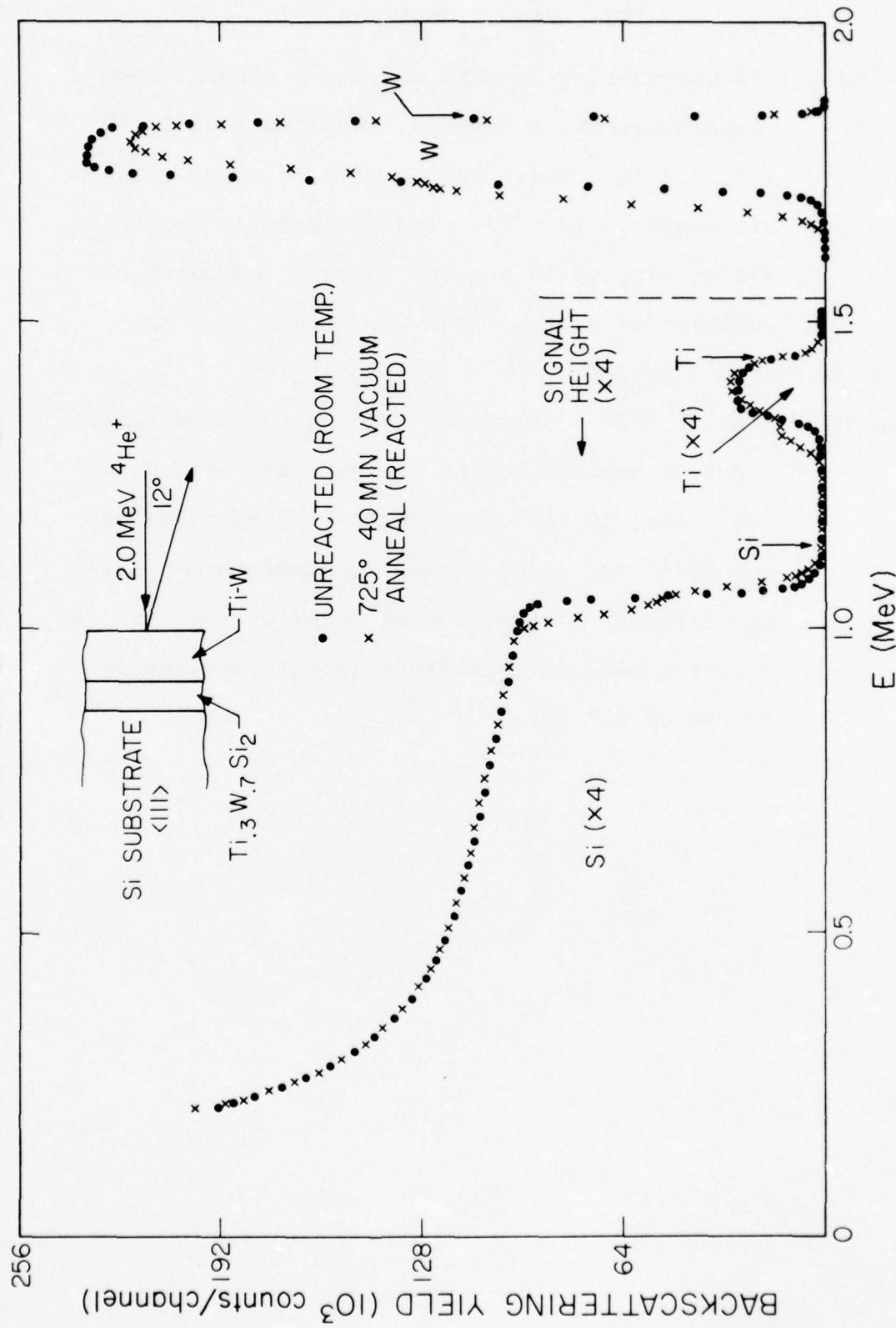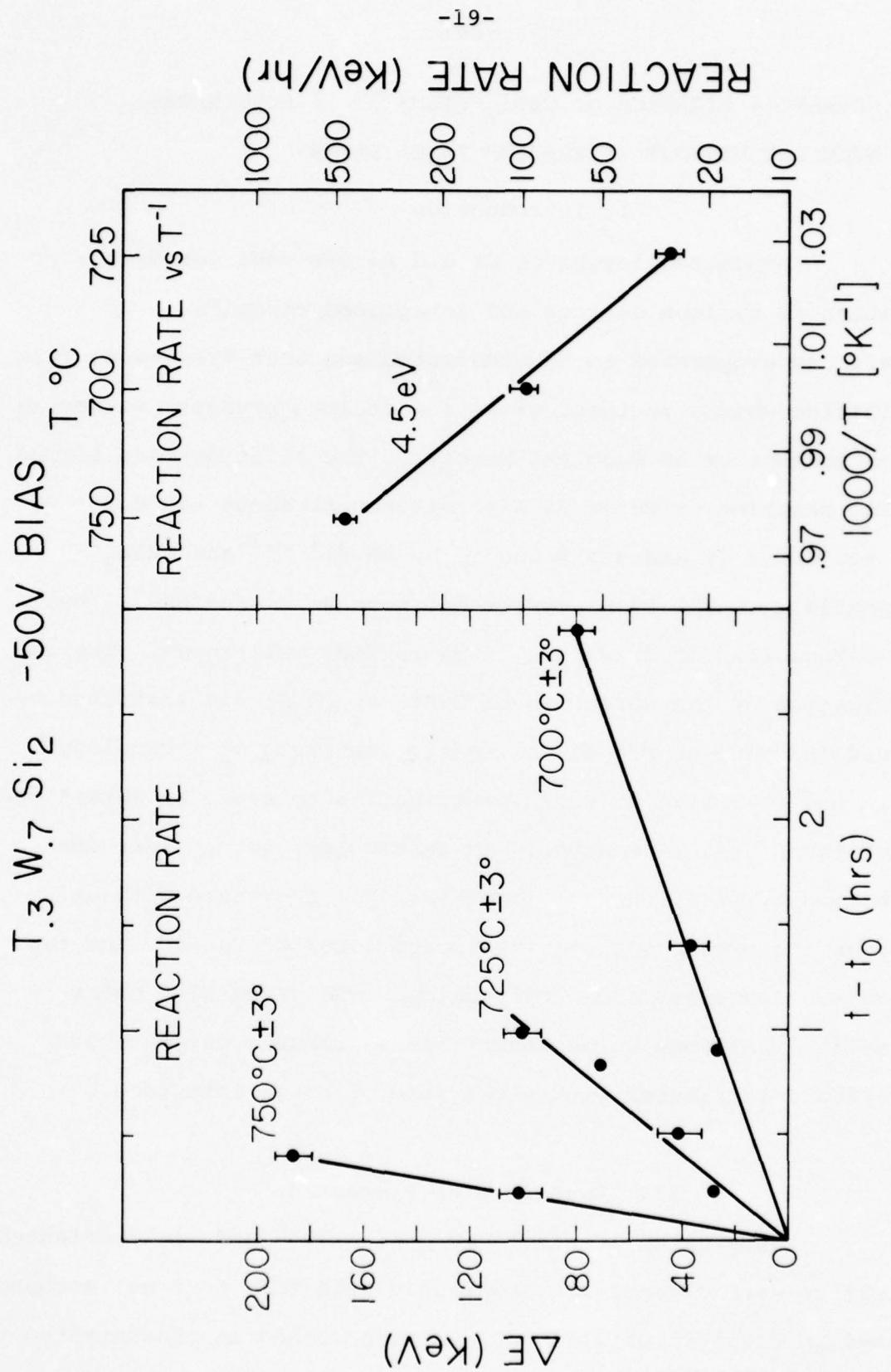
C. FORMATION KINETICS OF $CrSi_2$ FILMS ON Si SUBSTRATES

WITH AND WITHOUT INTERPOSED Pd_2Si LAYER

I. Introduction

Deposited layers of Cr and Pd are used for metallization in silicon devices and integrated circuits. The metals are evaporated on Si substrates and heat-treated to form a silicide which, in turn, gives the desired property either as ohmic contact or as Schottky barrier. The silicides are formed by the reaction of Pd or Cr with silicon at about 200°C for Pd and 450°C for Cr and are known to be Pd_2Si[1,2,3] and $CrSi_2$[1] respectively. The Pd-Si system has been well studied[1-5], but the interaction of Cr with silicon is less well known. The investigation of the formation of $CrSi_2$ on Pd_2Si was initiated by Sigurd and Van der Weg at California Institute of Technology[6]. It is the objective of this investigation to study in detail the kinetics of $CrSi_2$ formation. In particular, we consider the formation of $CrSi_2$ on a Si single-crystal substrate with or without the presence of an interposed layer of Pd_2Si. The two cases are discussed separately below. The study also underlines the influence which impurities - probably oxygen - can have when distributed within the film or at an interface.

II. Experimental Procedures

Substrates of single crystal <100>- and <111>-oriented Si wafers were cleaned ultrasonically with TCE, acetone, methanol, rinsed in doubly-distilled H_2O and then etched in concentrated

HF acid and rinsed again in doubly-distilled H_2O just before loading in the vacuum evaporator. Some of the samples were boiled in HNO_3, etched in HF and rinsed in H_2O before evaporation. Cr films of about 800 to 2000 Å were evaporated on single crystal Si, and Pd films ranging from 300 to 3000 Å were deposited on single crystal Si before Cr was evaporated on top. Whenever both Pd and Cr films were deposited on a Si wafer, both evaporations were made sequentially without breaking vacuum. All depositions were made with an electron gun in an oil-free deposition system. A vacuum of better than 2×10^{-6} torr was maintained during evaporation.

Heat treatments were performed in a vacuum annealing furnace. The vacuum was maintained at a pressure between 5 and 9×10^{-7} torr with an oil diffusion pump baffled with LN_2 trap. Most of the Si-Cr and Si-Pd-Cr samples were heat-treated together so that the resultant silicide thicknesses could be compared for identical process temperatures and times. Annealing temperatures ranged from 400°C to 525°C and lasted from about 10 to 150 minutes.

The product of the reaction of the Cr and Pd films with the substrates and the rate of growth of the $CrSi_2$ were measured with 2 MeV $^4He^+$ backscattering spectrometry. Observations with a scanning electron microscope (SEM) indicated that the samples investigated were laterally uniform. Read camera glancing angle X-ray diffraction techniques were used to identify the silicide phases.

III. Results and Discussion

A. Behavior of Cr films on single-crystal Si; linear and non-linear growth of $CrSi_2$.

Figure 1 shows 2 MeV $^4He^+$ backscattering spectra for samples with 2000 Å Cr evaporated on <100>-oriented Si substrates, annealed at 450°C for 50 minutes, and unannealed. The average atomic ratio of Si to Cr in the compound layer was determined to be 2 to 1 within ±10%, using the appropriate energy loss factors and differential scattering cross sections[7,8]. Read camera[9] X-ray analysis confirms that the compound layer is indeed $CrSi_2$. That the silicide, $CrSi_2$, forms under these conditions was also reported by Bower et al[1]. The compound phase develops at 450°C and is known to be stable beyond 1000°C. Measurements similar to those shown in Figure 1 were made for different times and temperatures and the thickness of $CrSi_2$ vs. annealing time was plotted as shown in Figure 2. The linearity of the growth of $CrSi_2$ with time indicates that the process is limited by the silicide reaction. This observation is also consistent with that reported by Bower et al[1]. It is worth noting also that $MoSi_2$ and VSi_2 exhibit the same linear type of growth[1,10,11]. Samples of thin Cr films evaporated on <100>- and <111>-oriented single crystal Si were annealed side by side together in a vacuum furnace at 500°C for times up to 60 minutes. At this temperature and times, we observed no substrate orientation effect on the growth of $CrSi_2$. This non-dependence of $CrSi_2$ growth on the orientation of the substrate has been

reported for Pd_2Si[2] and VSi_2[11], while the growth of Ni_2Si has been shown to be strongly dependent on the state of the sub-strates[12].

From the linear regime of Figure 2, the Arrhenius plot shown in Figure 3 was derived (open circles). The plot reveals a thermally activated process with an activation energy of E_a = 1.7 $\pm$ 0.1 eV. This value coincides with that of 1.7 eV $\pm$ 0.2 eV quoted for the growth of VSi_2[10].

Bower et al[1] report on samples annealed at 450°C for times up to only about 25 minutes and find growth which is linear in time. We have observed that for longer anneals (e.g. 80 minutes at 450°C) at all temperatures investigated, a nonlinear growth regime exists as shown (Figure 2). This non-linear behavior is attributed to contaminations introduced during annealing, and most probably oxygen or water vapor. That choice is suggested by the very similar observations made by Krautle et al[10] for VSi_2, and where oxygen was shown to cause nonlinear growth. In the presence of a substrate such as Si, backscattering spectrometry is insensitive to oxygen. An amount of oxygen sufficient enough to retard the reaction could easily escape detection.

To investigate the presence of light impurities in the Cr film, an experiment was performed in which about 800 Å of Cr was re-evaporated on a partly reacted film in which the top layer of about 500 Å Cr was still unreacted. The Cr signal obtained by backscattering spectrometry from this sample was

then compared with the Cr signal of an unannealed Si-Cr (solid line) sample (see Figure 4). The unreacted part of the Cr film generates a signal of smaller height than that of the unannealed sample, while the signal height of the freshly evaporated Cr layer agrees quite well with that of the unannealed sample (solid line in Figure 4). The decrease in yield of the unreacted part of Cr confirms that the Cr film is indeed contaminated. About 12-15% oxygen distributed uniformly in the unreacted portion of the Cr film is required to account for the reduction in the yield. The dip between the unreacted and the unannealed spectra is probably due to a layer of Cr oxide formed on the surface of the unreacted Cr.

B.   Behavior of Cr Films on Pd Films on Single Crystal Si.

Pd films of thicknesses between 300 and 3000 Å were vacuum-deposited on <100>-oriented Si and Cr films of thicknesses between 800 and 2000 Å were in turn evaporated on the Pd film without breaking vacuum. Typical backscattering spectra of such a sample with about 1400 Å Pd and 1200 Å Cr before and after annealing at 280°C for 60 minutes are shown in Figure 5. Palladium silicide (Pd_2Si) is known to form at about 200 to 300°C[2]. Annealing the Si-Pd-Cr sample at 280°C for 60 minutes has, there-fore, resulted in the formation of Pd_2Si (shaded region in Figure 5) without any noticeable interaction of Pd with Cr. Samples annealed subsequently at about 400°C develop a compound layer, at the Pd_2Si-Cr interface, identified by Read camera

glancing angle X-ray diffraction to be $CrSi_2$. The same results are obtained for samples heat-treated directly at 400°C. This silicide layer increases in thickness with increase in temperature at constant time, or with increasing time for a given temperature. Figure 6 shows a backscattering spectrum of a sample identical to that of Figure 5, but annealed at 450°C for 20 minutes. A compound layer has developed at the Pd_2Si-Cr interface, as indicated by a step on the high energy edge of the Si signal and a corresponding plateau at the low energy side of the Cr signal. Comparing Figures 5 and 6, we observe that the thickness of Pd_2Si layer remains unchaged as $CrSi_2$ grows on top. Figure 7 shows parts of three spectra for the same samples annealed at 475°C for 7, 10 and 15 minutes. A plot of the $CrSi_2$ layer thickness vs. time gives the growth kinetics of this process (see Figure 8). As for the Si-Cr system, the growth of $CrSi_2$ is linear with time, indicating that the process is reaction-limited. Again, a nonlinearity is observed at long annealing times which is attributed to contamination, with oxygen as a prime suspect. A plot of the reaction rate vs. reciprocal temperature gives an activation energy of 1.7 ± 0.1 eV (see Figure 3) which is the same value obtained for $CrSi_2$ on Si. This indicates that the intermediate layer of Pd_2Si does not affect the mechanism responsible for the growth process of $CrSi_2$. For both Si-Cr and Si-Pd-Cr samples, the $CrSi_2$ thicknesses are almost equal at temperatures where they can be compared. For example the $CrSi_2$ thickness is about 1500 Å at 450°C for

40 minutes in both cases, which corresponds to a formation rate of about 0.7 Å/sec.

To investigate the effect of the thickness of Pd_2Si on the growth rate of $CrSi_2$, Pd films of different thicknesses were evaporated on single crystal Si and Cr was sequentially evaporated on top. The thickness of Cr was such that it would not be completely reacted in the process of $CrSi_2$ formation at the temperatures and times chosen for the experiment (400°C for 20 minutes, 450°C for 30 minutes and 475°C for 15 minutes). A plot of $CrSi_2$ thickness vs. Pd_2Si thickness is shown in Figure 9. Within the experimental error the thickness of $CrSi_2$ remains constant regardless of the thickness of Pd_2Si. This gives further proof that the formation of $CrSi_2$ is independent of the presence or absence of Pd_2Si. The only limiting process is the reaction of Si with Cr.

In Figure 9 a point plotted for the reaction of Cr on bare Si (no Pd_2Si) at 400°C for 120 minutes indicates zero thickness of $CrSi_2$ (point at origin). No measurable $CrSi_2$ thickness was observed also for Pd-free samples annealed at 425°C. Another point in the plot gives the amount of $CrSi_2$ measured on the Pd-free sample when it is annealed first at 500°C for 3 minutes and then annealed for 120 minutes at 400°C. There was no measurable amount of $CrSi_2$ after the quick treatment at 500°C for 3 minutes but during the subsequent annealing at 400°C for 120 minutes a $CrSi_2$ layer was formed which was almost of the same thickness as the $CrSi_2$ layer formed at 400°C

in the presence of some Pd_2Si. The absence of a reaction of Cr on bare Si at 400°C can thus be overcome by a quick exposure to higher temperature. We suspect that the effect is due to contamination at the Cr-Si interface such as a thin oxide layer. The oxide layer may not withstand the brief thermal shock at 500°C. There is no corresponding effect of the oxide layer in the presence of Pd_2Si. We think that this is due to the elimination of the original interface by the formation of Pd_2Si at a relatively low temperature. This method of cleaning the interface by silicide formation at low temperature has been exploited also in the solid-phase epitaxial growth of Si through Pd_2Si[13].

IV. Conclusion

We have investigated the properties and the rate of formation of $CrSi_2$ from evaporated thin films of Cr on Si single crystals, by using a 2 MeV $^4He^+$ backscattering spectrometry. For both Si-Cr and Si-Pd-Cr samples, the rate of $CrSi_2$ formation is the same, and is linear in time with an activation energy of 1.7 ± 0.1 eV. For each temperature, the rate slows down and becomes nonlinear at long annealing times. The effect has been proved to be due to a contaminant distributed uniformly in the Cr film, most probably oxygen.

Those systems were investigated for temperatures between 400°C and 525°C and times up to 2-1/2 hours. There is formation of Pd_2Si in the Si-Pd-Cr system at about 280°C and

$CrSi_2$ starts to form at about 400°C. No $CrSi_2$ formation was observed for Si-Cr below 450°C. The absence of $CrSi_2$ in the Si-Cr reaction below 450°C is attributed to the presence of an interfacial layer between the Cr film and Si substrate, quite probably a thin oxide layer.

Samples prepared with different thicknesses of Pd_2Si all show the same thickness of $CrSi_2$ after the same annealing. This independence of the $CrSi_2$ formation on the existence of a Pd_2Si layer proves that the formation of $CrSi_2$ is only limited by Si-Cr reaction.

V. References

* Work supported in part by Air Force Cambridge Research Laboratories (D.E. Davies) and the Gulf Oil Foundation (A. Lewis, Jr.).

1. R. W. Bower and J. W. Mayer, Appl. Phys. Lett. 20, 359 (1972).

2. R. W. Bower, D. Sigurd and R. E. Scott, Solid-State Electron. 16, 1461 (1973).

3. W. V. T. Rush and C. A. Burrus, Solid-State Electron. 11, 517 (1968).

4. C. J. Kircher, Solid-State Electron. 14, 507 (1971).

5. W. D. Buckley and S. C. Moss, Solid-State Electron. 15, 1331 (1972).

6. D. Sigurd and W. Van der Weg, California Institute of Technology (unpublished).

7. J. F. Ziegler, Thin Solid Films 19, 289 (1973).

8. J. F. Ziegler and W. K. Chu, Atomic Data and Nuclear Data Tables 13, 463 (1974).

9. S. S. Lau, W. K. Chu, J. W. Mayer and K. N. Tu, Thin Solid Films 23, 205 (1974).

10. H. Krautle, M-A. Nicolet and J. W. Mayer, J. Appl. Phys. 45, 3304 (1974).

11. J. W. Mayer and K. N. Tu, J. Vac. Sci. Technol. 11, 86 (1974).

12. J. O. Olowolafe, M-A. Nicolet and J. W. Mayer, Thin Solid Films (in press).

13. C. Canali, S. U. Campisano, S. S. Lau, Z. L. Liau and J. W. Mayer, J. Appl. Phys. 46, 2831 (1975).

VI. Figure Captions

Figure 1. $^{4}He^{+}$ backscattering spectrum of 2000 Å Cr film evaporated on Si <100>, before (solid dots) and after (open circles) annealing at 450°C for 50 minutes.

Figure 2. Thickness, W, of $CrSi_2$ formed in the reaction between Cr and Si <100> single crystal as a function of time. The nonlinear regime is due to contamination, with oxygen as a prime suspect.

Figure 3. Arrhenius plot for $CrSi_2$ formation in the reaction of Cr with Si <100> single crystal (open dots) and on Pd_2Si grown on Si <100> single crystal (solid dots).

Figure 4. $^4He^+$ backscattering spectrum of a 2000 Å Cr on Si <100>

single crystal, annealed at 450°C for 60 minutes and

then vacuum-deposited about 800 Å Cr on top (open

circles). The solid line is the unannealed sample.

About 12-15% oxygen contamination has resulted in the

decrease in the yield of the unreacted Cr layer. The

dip between the unreacted and the evaporated layers is

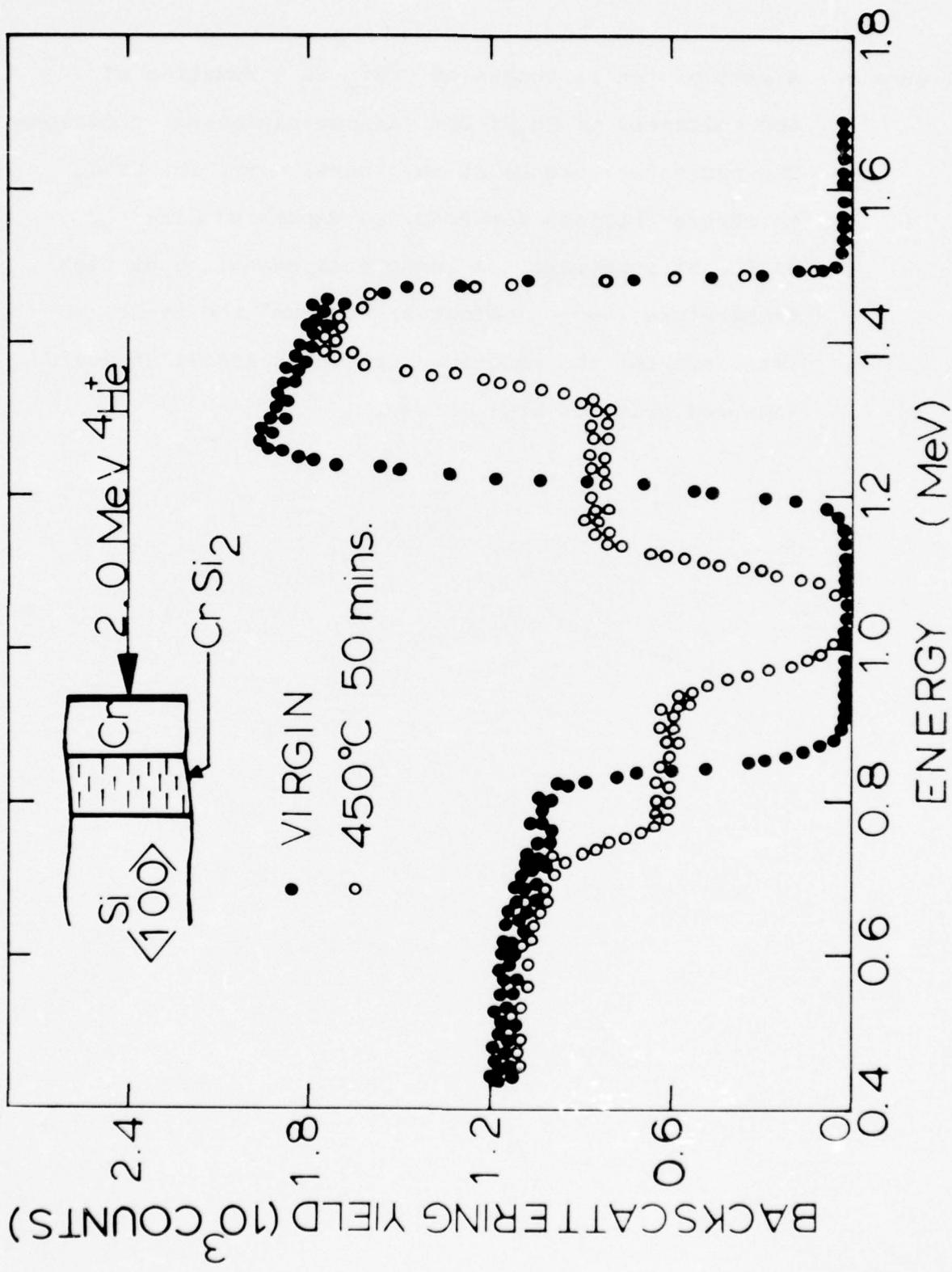likely due to a thin oxide layer on the vacuum-annealed

sample. Samples were tilted 45° with respect to beam.

Figure 5. $^4He^+$ backscattering spectrum of Pd (1400 Å) and Cr

(1200 Å) evaporated in that order on Si <100> single

crystal before (top) and after (bottom) annealing at

280°C for 60 minutes. The reaction between Pd and Si

results in the formation of Pd_2Si while there is
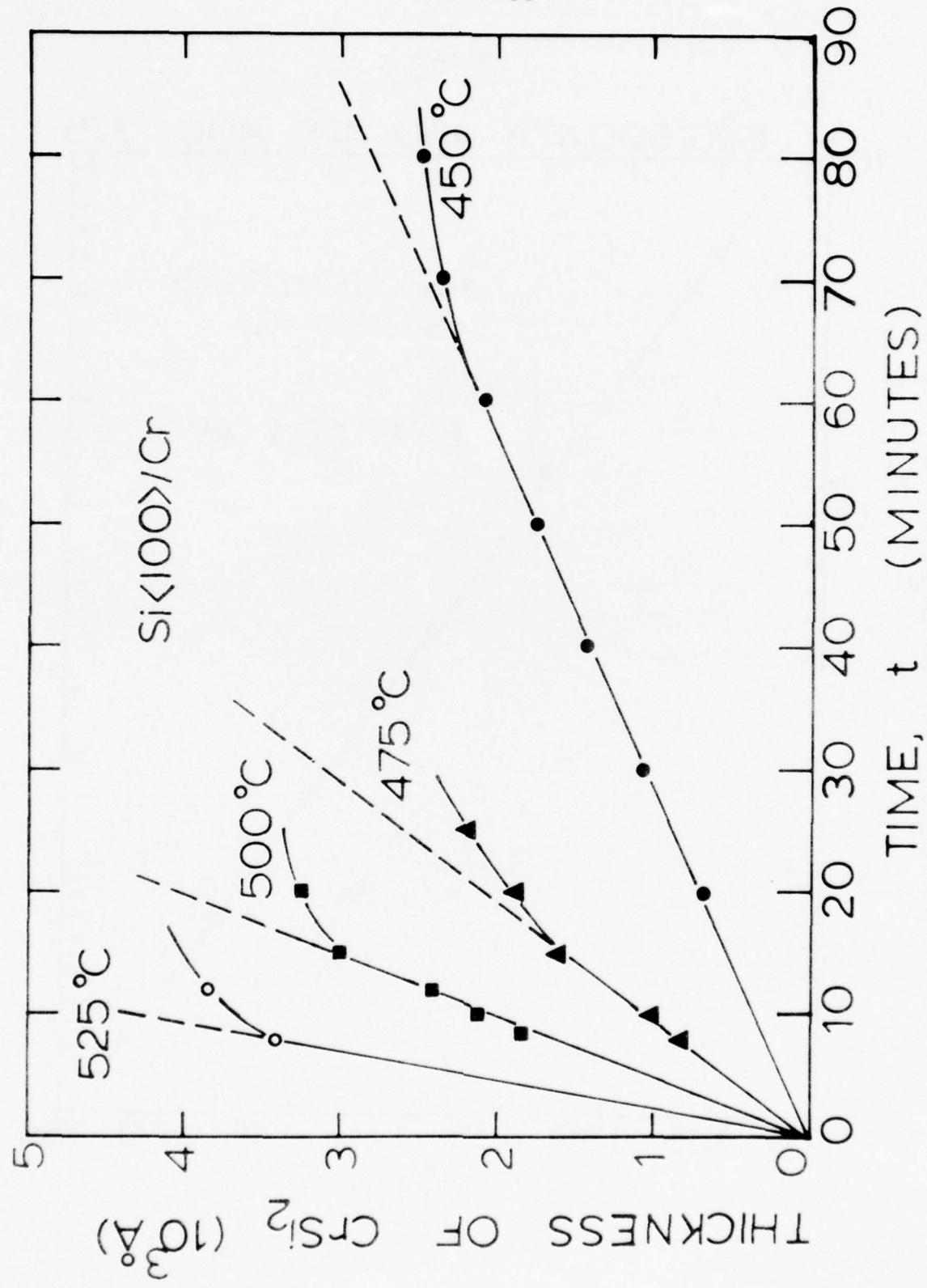
no apparent interaction between Pd and Cr.

Figure 6. $^4He^+$ backscattering spectrum of Pd (1400 Å) and

Cr (1200 Å) evaporated in that order on Si <100>

single crystal and annealed at 450°C for 20 minutes.

All Pd has reacted with Si to form Pd_2Si before

$CrSi_2$ was formed on top.

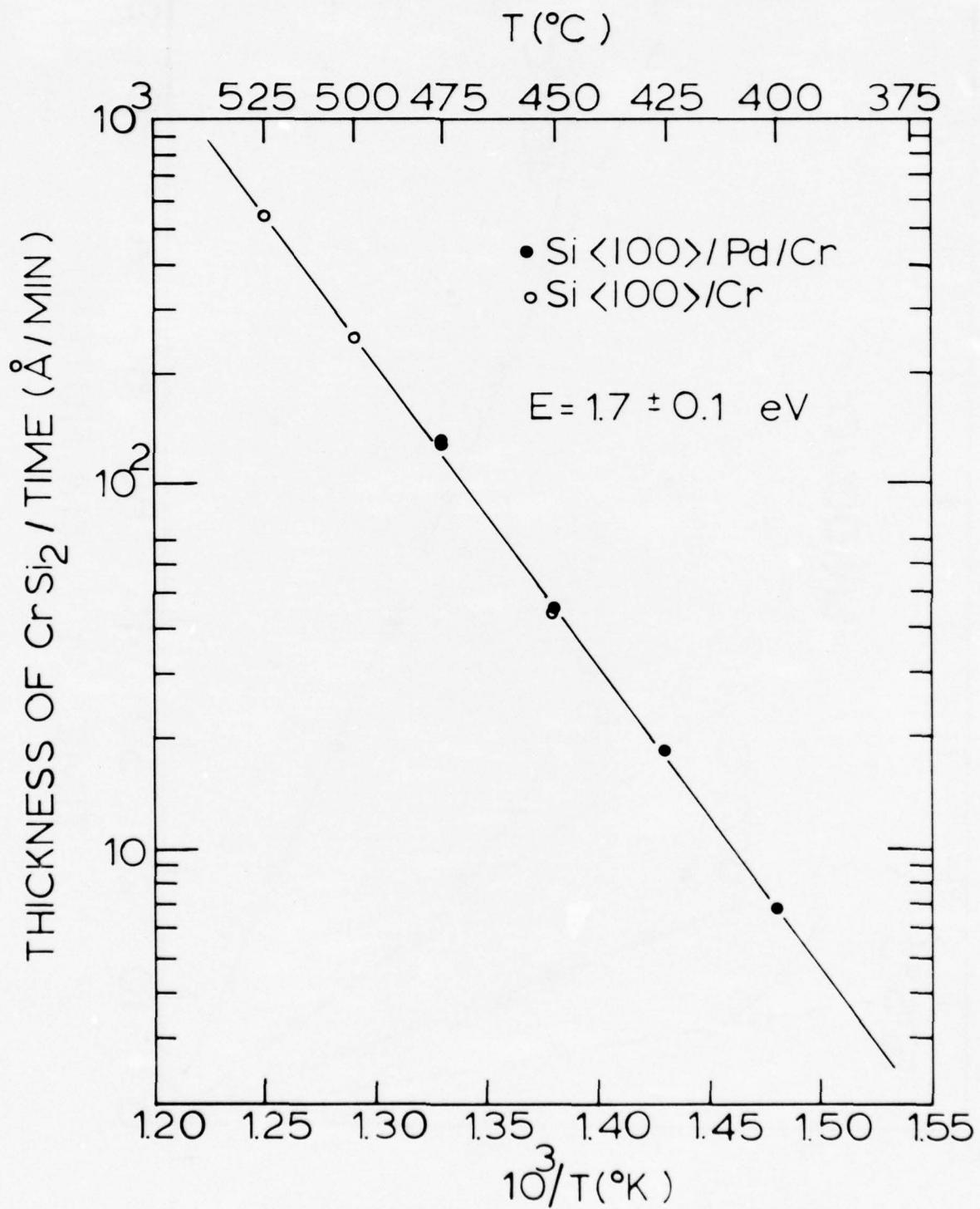Figure 7. $^4He^+$ backscattering spectrum of isothermal growth

of $CrSi_2$ on top of Pd_2Si. Anneals were done at
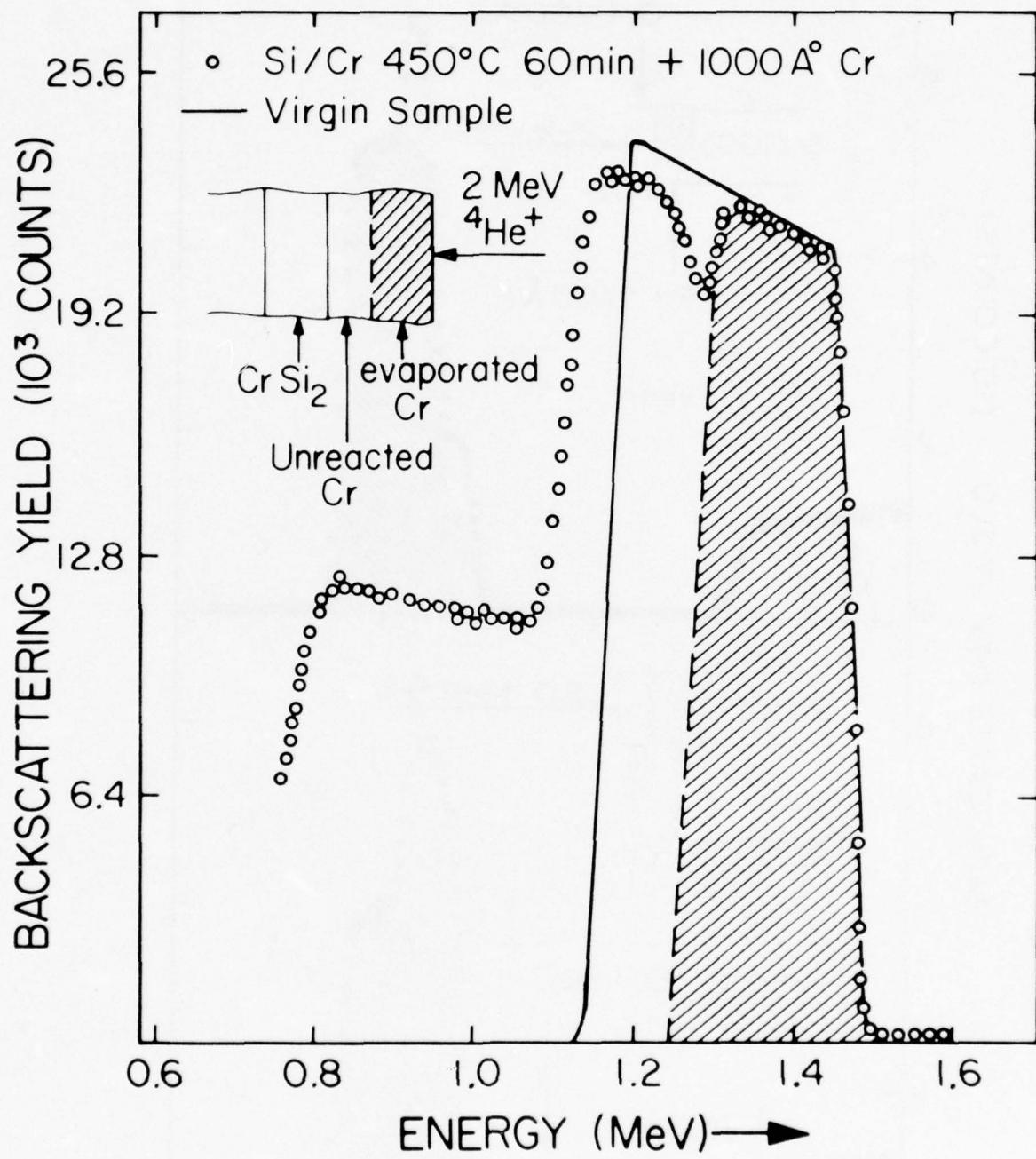
475°C for 7, 10, and 15 minutes.

Figure 8.   Thickness, W, of $CrSi_2$ formed on Pd_2Si grown on

Si <100> single crystal as a function of time. The

nonlinear regime is attributed to oxygen contamination.
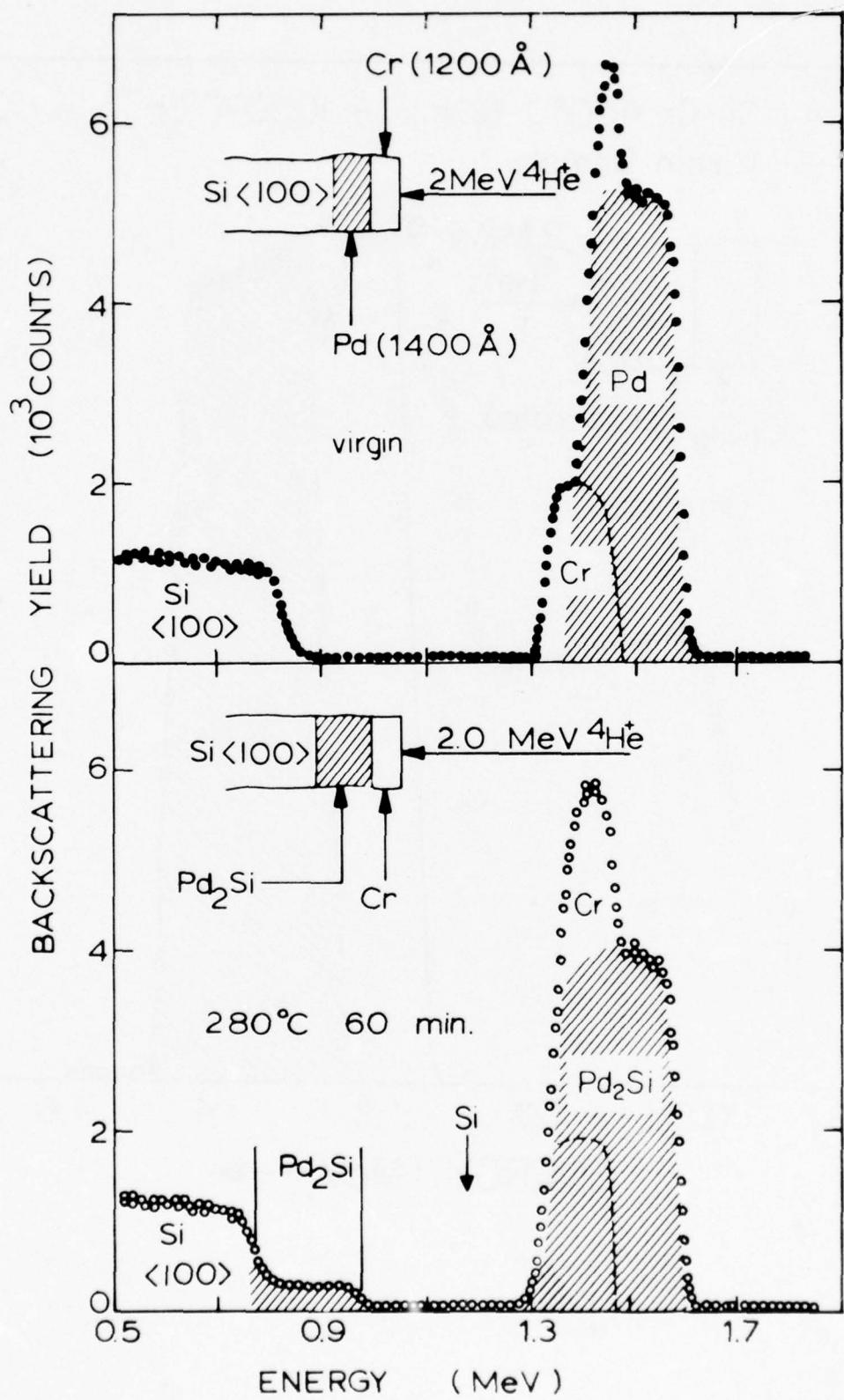
Figure 9. A plot of the thickness of $CrSi_2$ as a function of the thickness of Pd_2Si for various annealing conditions. The ordinate (zero Pd_2Si thickness) gives the $CrSi_2$ thickness obtained for Cr films deposited directly on the Si substrate. A short-time annealing at high temperature (500°C 3 minutes) "cleans" the Si-Cr interface for the reaction between Cr and Si at 400°C (arrowed point on $CrSi_2$ axis).

THICKNESS OF Pd₂Si (Å)

475 °C 15 min.

450°C 30min.

400°C 120 min.

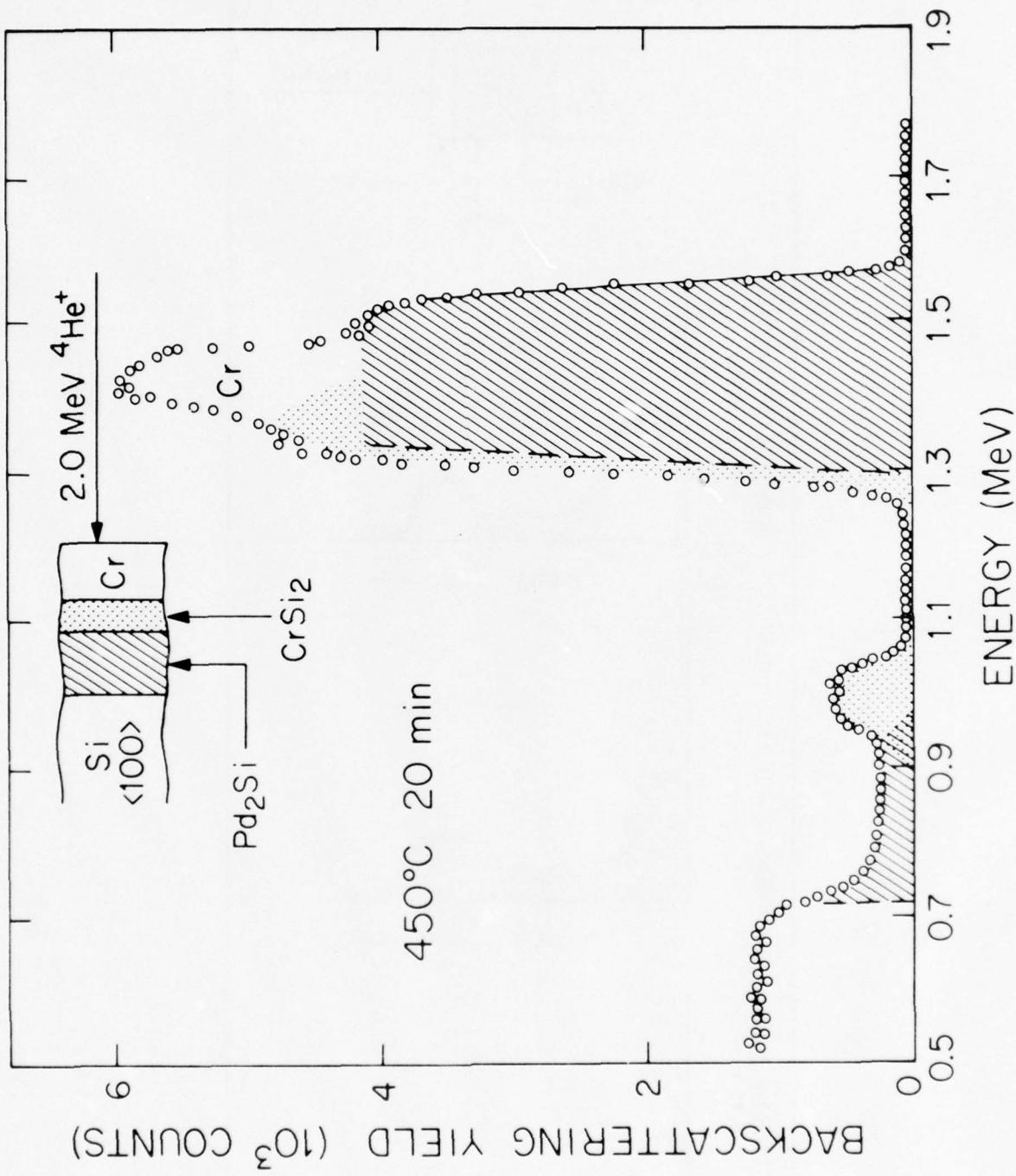500°C 3min.+ 400°C 120 min.

THICKNESS OF CrSi₂ (Å)

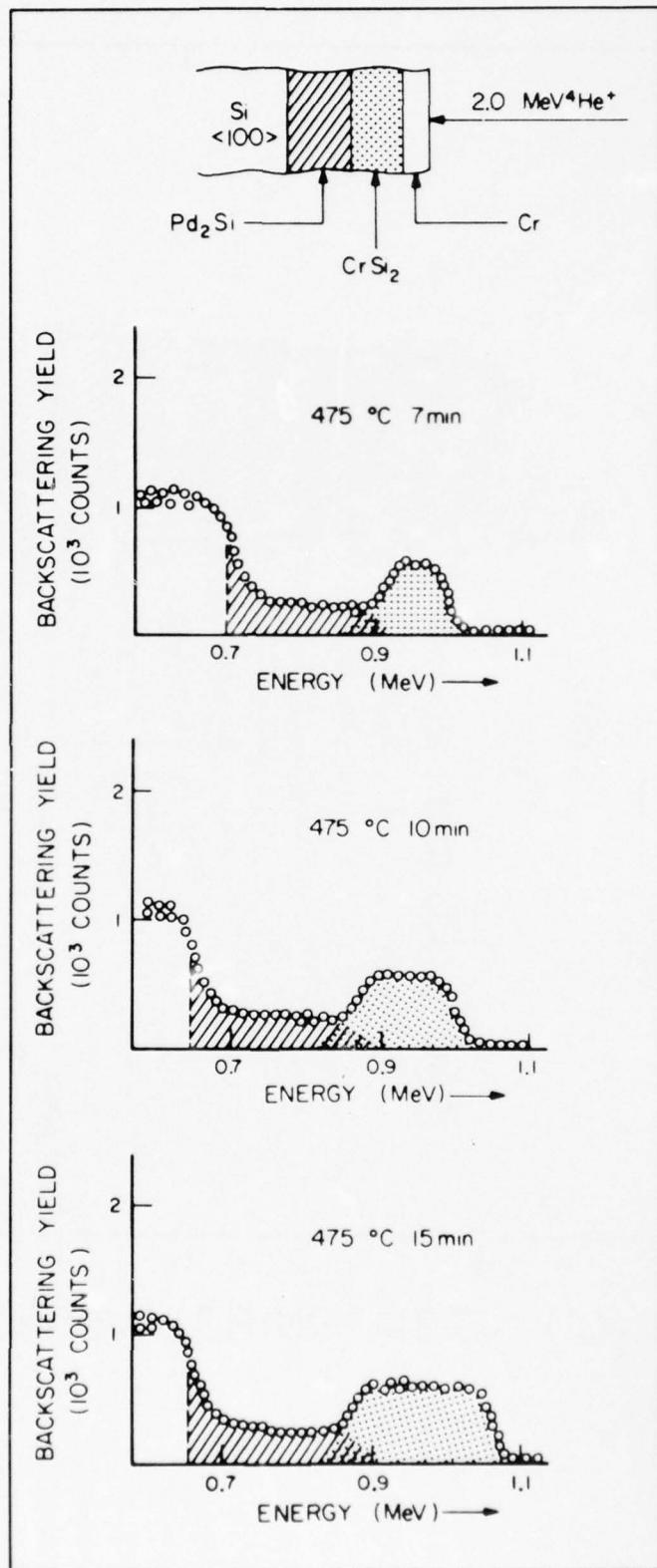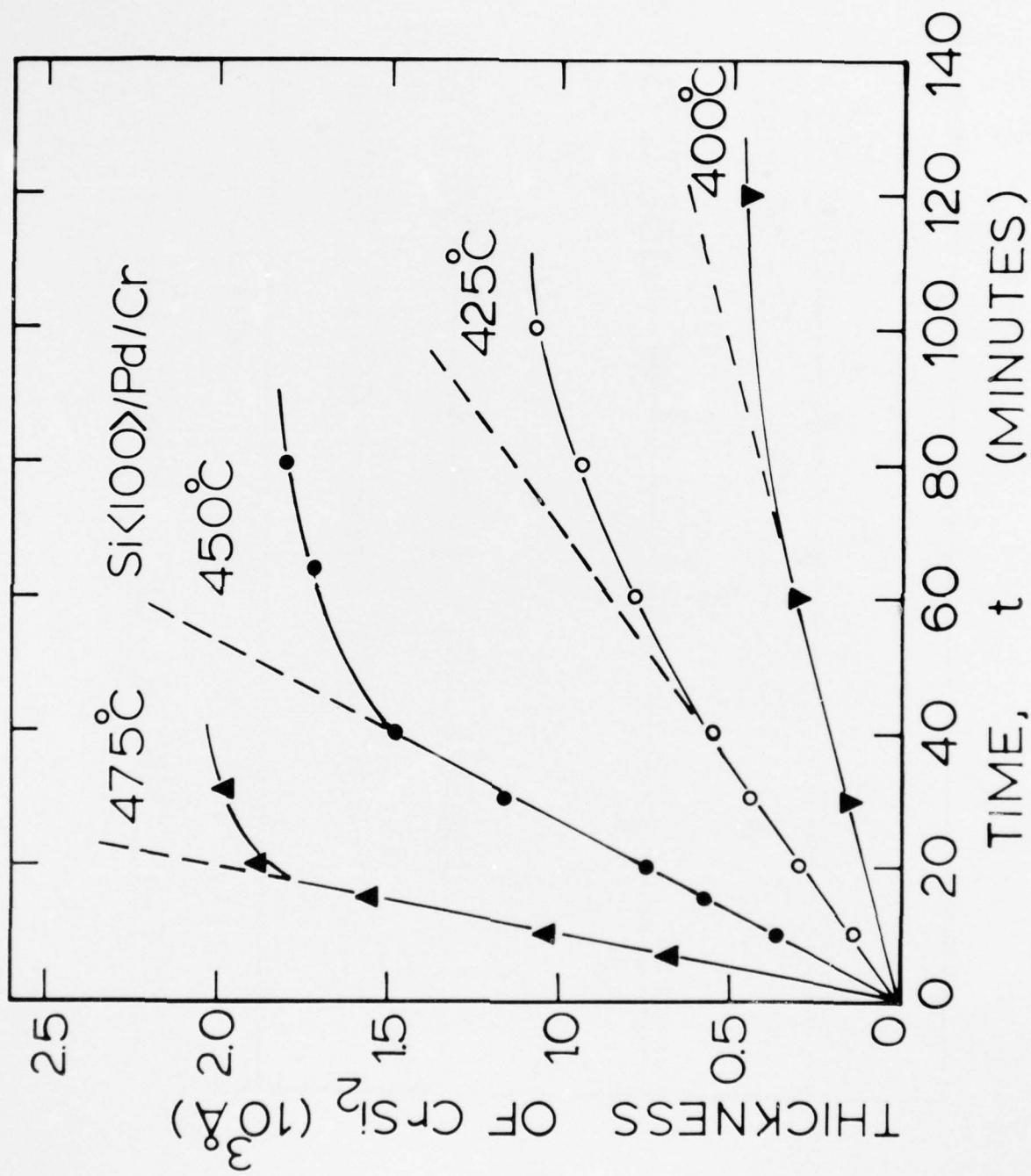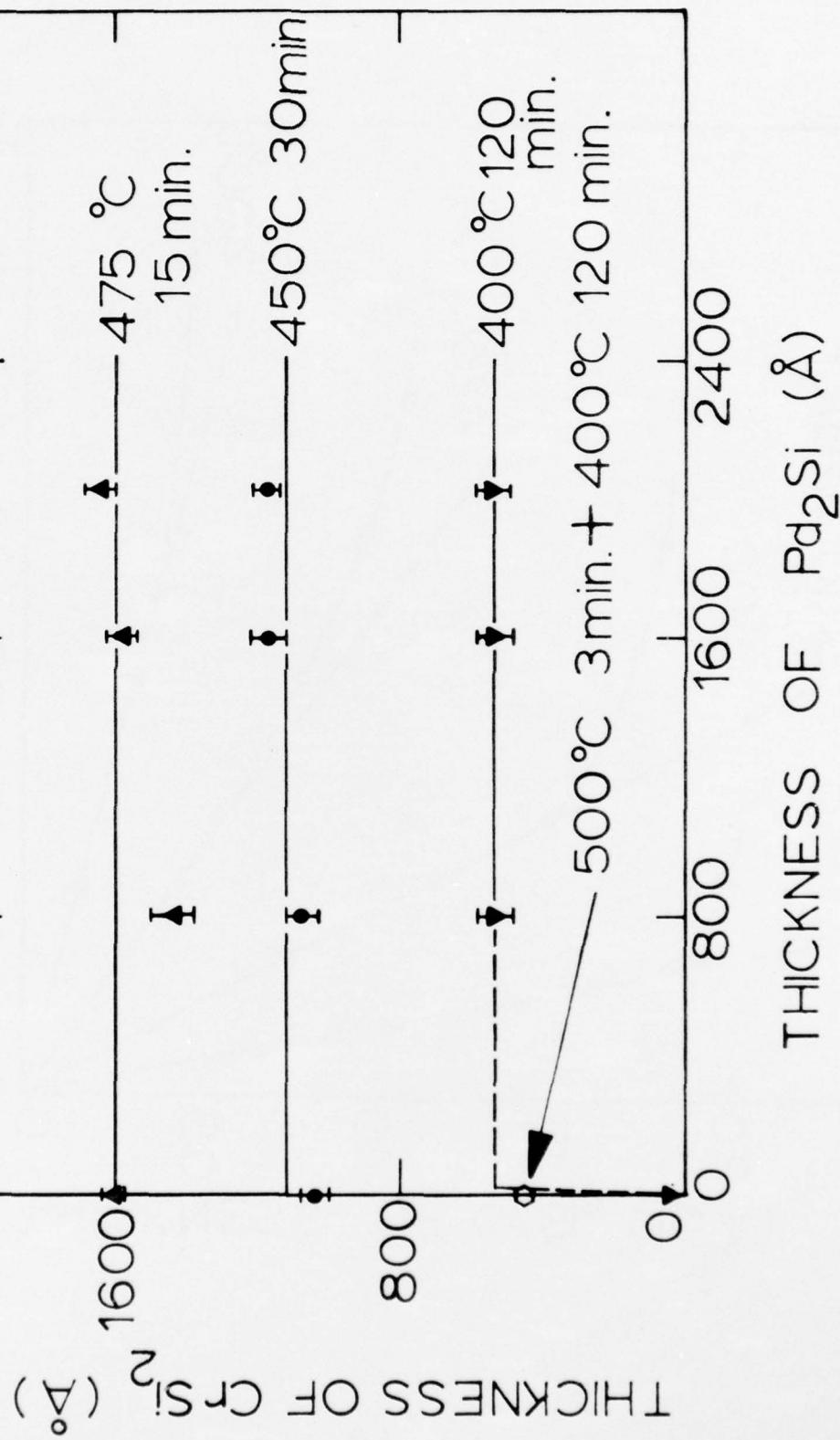1600

800

0

0   800   1600   2400

D.   CHROMIUM THIN FILM AS A BARRIER TO THE INTERACTION OF
     Pd_2Si WITH Al*

I.   Introduction

Palladium silicide is widely used as a Schottky
barrier and Al as a metallization layer in silicon integrated
circuits (IC's). Data on the rate of formation and structural
properties of Pd_2Si have been reported [1-4]. A single phase
of Pd_2Si forms at temperatures below 800°C. The electrical
properties (barrier heights, contact resistance, etc.) of
this silicide have also been measured [2,3,5].

Heat treatment of Al films on Si substrates at
temperatures conducive to IC metallization results in the
migration of Si into the overlying Al layer [6-8]. When the
Al film is in contact with the Si substrate at selected
locations,   as is typically the case in IC's,   Si dis-
solution occurs nonuniformly. Heavy localized erosion of the
Si substrate results. Bower [9] has used a Ti layer between
Si and Al to prevent this pitting. The Ti film reacts, in
a predictable fashion, with the Al film but not with the Si
substrate. As long as/the Ti layer is not totally consumed in
the Ti-Al reaction, an effective separation of Al and Si is
maintained and the integrity of the Si substrate is preserved.
In a similar way, Nakamura et al. have deferred the recrystal-
lization of polycrystalline Si (poly Si) in contact with an
Al film by placing a buffer layer of V or Ti between the poly

Si and the Al film [10]. Here again, the buffer layer reacts selectively with the Al only, and the poly Si remains intact as long as the buffer film is not fully consumed by this reaction.

Wittmer, et al. have worked on the interaction of Al films with Pd_2Si layers on single-crystal Si substrates [11]. They show that upon annealing the $Si-Pd_2Si-Al$ samples between 300 and 450°C the Al reacts with the Pd_2Si which results in a nonuniform erosion of the interface between the Pd_2Si and the Si substrates. They chemically removed the interdiffused Pd_2Si-Al layer to expose this interface. Scanning electron micrographs revealed a nonuniform erosion of the Si substrate surface, similar in appearance to the Si-Al and the poly Si-Al metal cases mentioned earlier.

Motivated by these findings we have investigated the formation kinetics of $CrSi_2$ on Pd_2Si grown on <100> Si substrates [12]. The growth of the $CrSi_2$ proceeds at a linear rate with time, with an activation energy of 1.7 eV. Howard et al. report the kinetics of compound formation for the interaction of thin films of Cr with Al [13]. They state that the compounds $CrAl_7$ (for Al thickness greater than Cr thickness) and Cr_2Al_{11} (for Cr thickness greater than or equal to the Al thickness) form between 300 and 450°C. From these results one should expect that at about 400°C/Cr film the placed between layers of Pd_2Si and Al will react at both interfaces.

This work deals with a Pd-Al metallization scheme and shows how a thin Cr layer interposed between Pd and Al can be used to prevent Pd_2Si from interacting with Al and thereby preserve the integrity of the $Si-Pd_2Si$ interface. Backscattering spectrometry with 2.0 and 2.3 MeV $^4He^+$ is used to study the Pd_2Si-Al interaction, the interaction of Cr with Si and with Al, and to investigate the barrier effect of the $CrSi_2$ and $CrAl_x$ formed in the actual metallization scheme.

II. Experimental

All experiments were performed with single crystal <100> Si wafers as substrates. Samples were prepared by e-gun evaporation of 300 to 2000Å of Pd, followed by about 3000Å of Al evaporated on the Pd without breaking vacuum. On some samples only thin films of Pd were deposited, annealed in vacuum at temperatures ranging from 275 to 300°C to form Pd_2Si with all of the Pd before Al was vacuum deposited on top. Other samples were prepared with sequential evaporation of thin films of Pd and Cr or Pd, Cr and Al in a single pump-down. The vacuum during deposition was about 2×10^{-6} Torr. All substrates were cleaned ultrasonically with trichlorethylene, acetone, and methanol, followed by a rinse in double-distilled H_2O, diluted HF etch and again rinsed in a double-distilled H_2O just prior to evacuation. Some samples were cleaned in hot HNO_3 before a dilute HF etch. The results obtained for these samples are the same as those obtained for samples which were not cleaned with HNO_3.

Heat treatments were performed in a vacuum anneal furnace at a pressure of about 8×10^{-7} Torr. Temperatures were chosen between 275 and 550°C with times up to 2 hours. The heat treatments were essentially isothermal ($\pm$ 1°C).

The backscattering measurements were performed with a 2.0 and 2.3 MeV ^{4}He$^+$. Description of this analytical technique is available in a number of references [4,14,15]. The backscattering spectrum of a laterally nonuniform sample can be quite misleading. A scanning electron microscope was therefore used to observe the surface of the samples and check against lateral uniformities.

III. Results and Discussion

The backscattering spectrum with 2.0 MeV ^{4}He$^+$ of a sample with about 600$\overset{\circ}{A}$ of Pd_2Si plus 3500$\overset{\circ}{A}$ Al is shown in Fig. 1 (full dots). The sample was annealed at 450°C for 15 minutes and a second backscattering spectrum was taken (open circles). The annealed sample shows substantial interdiffusion of Pd_2Si and Al, which destroys the Si-Pd_2Si interface. The same situation occurs for Si-Pd-Al samples which were obtained by sequentially evaporating Pd and Al on Si and which were then annealed at 450°C for 15 minutes, as were the Si-Pd_2Si-Al samples. Since these changes during annealing are undesirable phenomena in Al metallizations, we have introduced a layer of Cr (300 to 1500$\overset{\circ}{A}$) between the Al and Pd_2Si.

Figure 2 shows the backscattering spectrum of a sample in which Pd and Cr were deposited, in that order, on a single crystal Si substrate and annealed at 450°C for 20 minutes. The spectrum shows that in the absence of Al, Cr reacts with Si and forms $CrSi_2$ on top of Pd_2Si. Both Pd_2Si and $CrSi_2$ are formed in distinct sublayers. Read Camera x-ray diffraction patterns confirm that both Pd_2Si and $CrSi_2$ are formed. Other samples heat-treated at 280°C for 60 minutes followed by 450°C for 20 minutes give similar results. The fact that these two types of annealing give the similar results is plausible because Pd_2Si forms at about 200°C while $CrSi_2$ does not form until about 450°C.

The backscattering spectrum with 2.3 MeV $^4He^+$ for a sample in which Pd, Cr and Al were sequentially evaporated on single crystal Si is shown in Fig. 3 before and after annealing at 450°C for 10 minutes. In this particular example, the layer thicknesses were about 800Å for Pd, 500Å for Cr and 3000Å for Al. These thicknesses were chosen for convenience of a clear interpretation of the backscattering spectra. The schematic representation of the two spectra is shown in Fig. 4. During the annealing, all of the Pd reacts with the Si substrate to form Pd_2Si. Chromium silicide, $CrSi_2$, is formed at the interface between Cr and Pd_2Si, and $CrAl_x$ compound at the interface between Cr and Al. At this temperature and time, not all the Cr is consumed in the reaction process and about 1200Å Al is still unreacted. We

have noted also that backscattering spectra of samples with thin layers of unreacted Cr show sharp boundaries.

For samples annealed up to 500°C and times not greater than 90 minutes, the integrity of Pd_2Si and of the interface between Si and Pd_2Si are maintained. Above this temperature or for longer annealing, the signals of $CrSi_2$ and $CrAl_x$ compound layers begin to overlap, thus making the backscattering spectra difficult to interpret. Under the microscope, one observed that the surface of the samples is no more smooth. The backscattering spectra indicate the presence of Pd and Al on the surface. Clearly, the Pd_2Si layer has undergone major alterations, the nature of which has not been investigated further.

IV. Conclusion

The destruction of the interface between Si and Pd_2Si when Pd_2Si is in contact with a Al film can be prevented by interposing a layer of Cr between Pd and Al. The thickness of our Cr layers ranged from 300 to 1500Å. During annealing, chromium reacts with Si to form $CrSi_2$ at the interface between Cr and Pd_2Si; it also reacts with Al at the Cr-Al interface and forms a $CrAl_x$ compound. As long as a layer of unreacted Cr is present, the integrity of the Pd_2Si layer on the Si substrate is preserved.

V. References

* Work supported in part by the Air Force Cambridge Research Laboratories (D.E. Davies) and by the Gulf Oil Foundation (A. Lewis, Jr.).

1. W.V.T. Rush and C.S. Burrus, Solid-St. Electron. 11, 517 (1968).

2. C.J. Kircher, Solid State Elec. 14, 507 (1971).

3. W.D. Buckley and S.C. Moss, Solid-St. Electron. 15, 1331 (1972).

4. R.W. Bower, D. Sigurd and R.E. Scott, Solid-St. Electron. 16, 1461 (1973).

5. A. Shepela, Solid-St. Electron. 16, 477 (1973).

6. J.O. McCaldin and H. Sankur, Appl. Phys. Lett. 19, 524 (1971).

7. A. Hiraki, E. Lugujjo, M-A. Nicolet and J.W. Mayer, Phys. Stat. Sol. A7, 401 (1971).

8. H. Sell, Elec. Chem. Soc., Ext. Abstr. 17, 2 (1968).

9. R.W. Bower, Appl. Phys. Lett. 23, 99 (1973).

10. K. Nakamura, S.S. Lau, M-A. Nicolet and J.W. Mayer, Appl. Phys. Lett. 28, 277 (1976).

11. M. Wittmer and R. Pretorius, California Institute of Technology, (unpublished).

12. J.O. Olowolafe, M-A. Nicolet and J.W. Mayer, to be published.

13. J.K. Howard, R.F. Lever, P.J. Smith and P.S. Ho, J. Vac. Sci. Tech. 13, 68 (1976).

14. S.S. Lau, W.K. Chu, J.W. Mayer and K.N. Tu, Thin Solid
    Films 23, 205 (1974).

15. W.K. Chu, J.W. Mayer, M-A. Nicolet, T.M. Buck, G. Amsel
   and F. Eisen, Thin Solid Films 17, 1 (1973).

VI. Figure Captions

Figure 1. 2 MeV ^{4}He$^+$ backscattering spectra of a sample con-
sisting of a layer of about 600Å Pd_2Si formed on a
single crystal <100>-oriented Si substrate and
covered with a film of 3500Å Al deposited on top
before (●) and after (o) annealing at 450°C for
15 min. in vacuum.

Figure 2. 2 MeV ^{4}He$^+$ backscattering spectra of a sample con-
sisting of Pd (1400Å) and Cr (1200Å) deposited in
that order on a single crystal <100>-oriented Si
substrate annealed at 450°C for 20 min. Both Pd_2Si
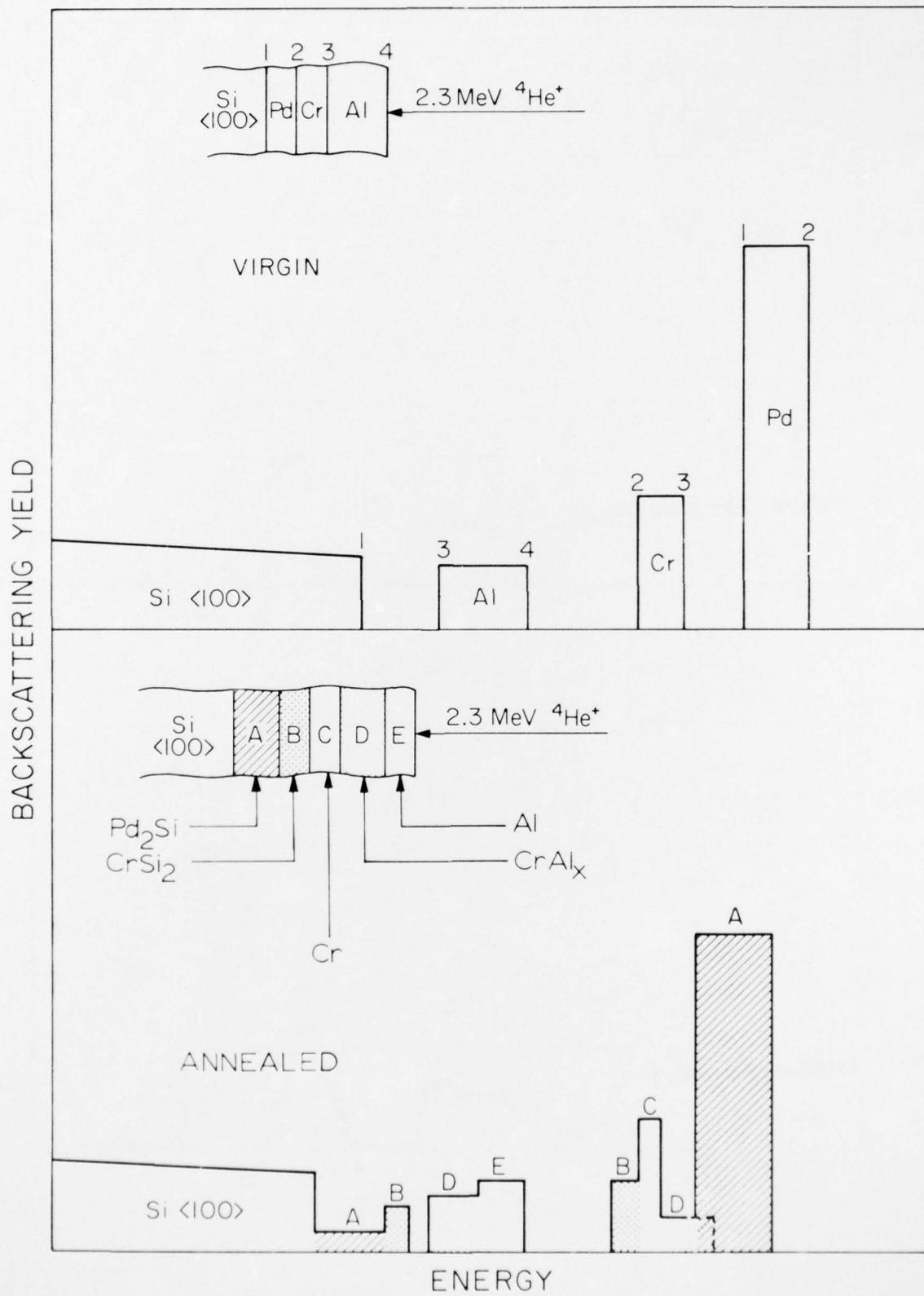and $CrSi_2$ are formed in distinct sublayers.

Figure 3. 2.3 MeV ^{4}He$^+$ backscattering spectrum of Pd, Cr and
Al layers deposited, in that order, on a single
crystal <100>-oriented Si substrate before (o) and
after (●) annealing at 450°C for 10 min.

Figure 4. Schematic representation of backscattering spectra
of Fig. 3.
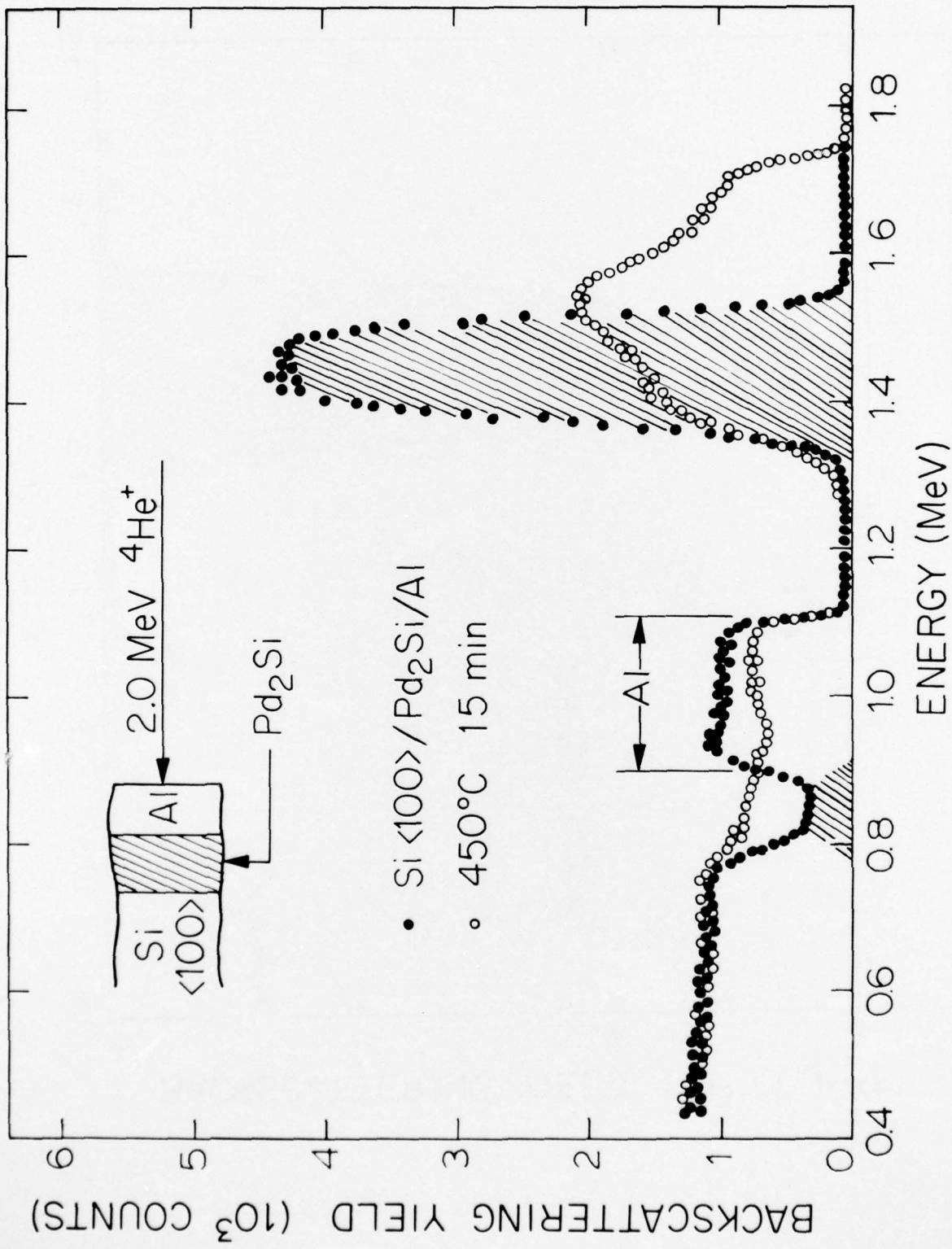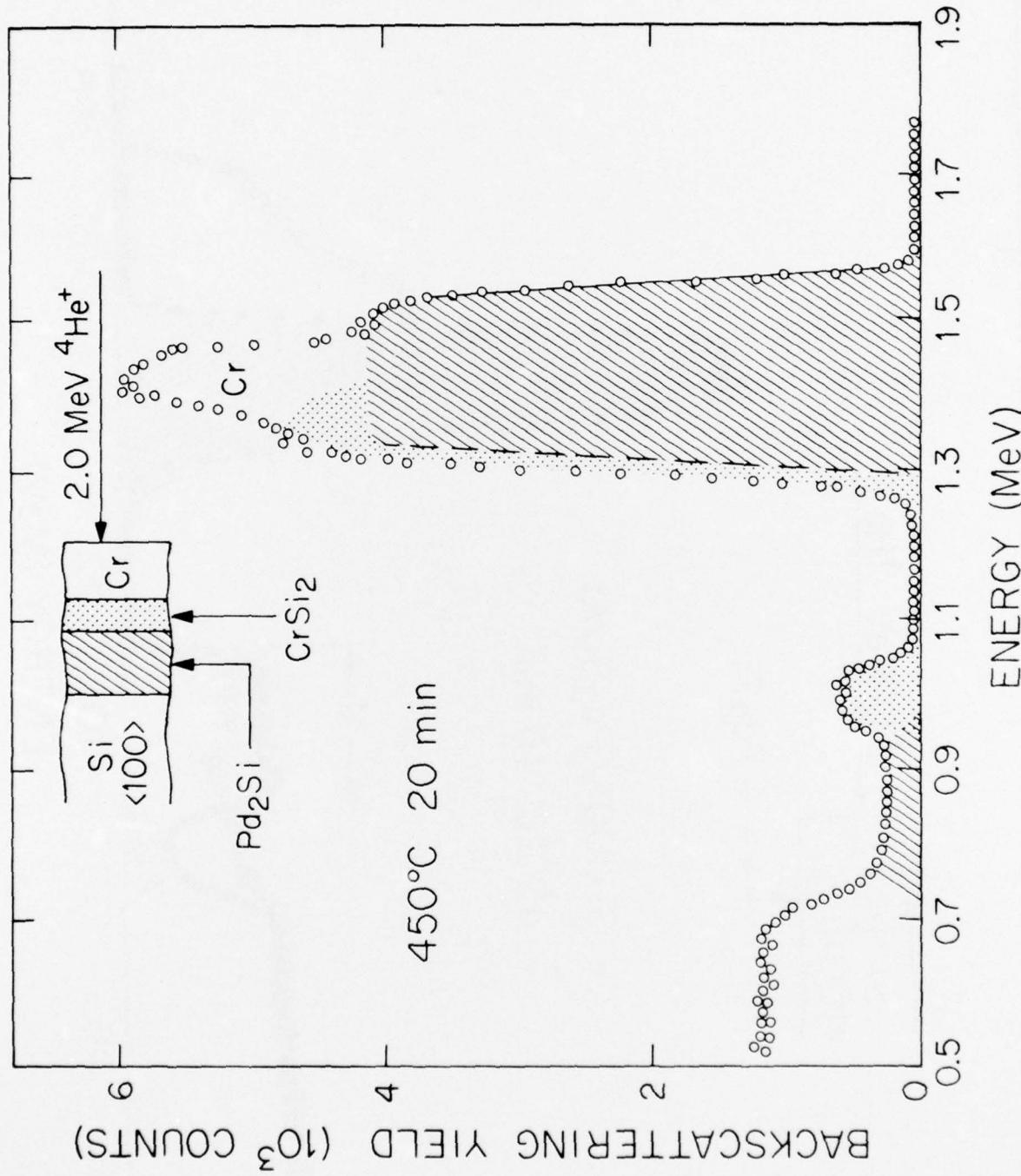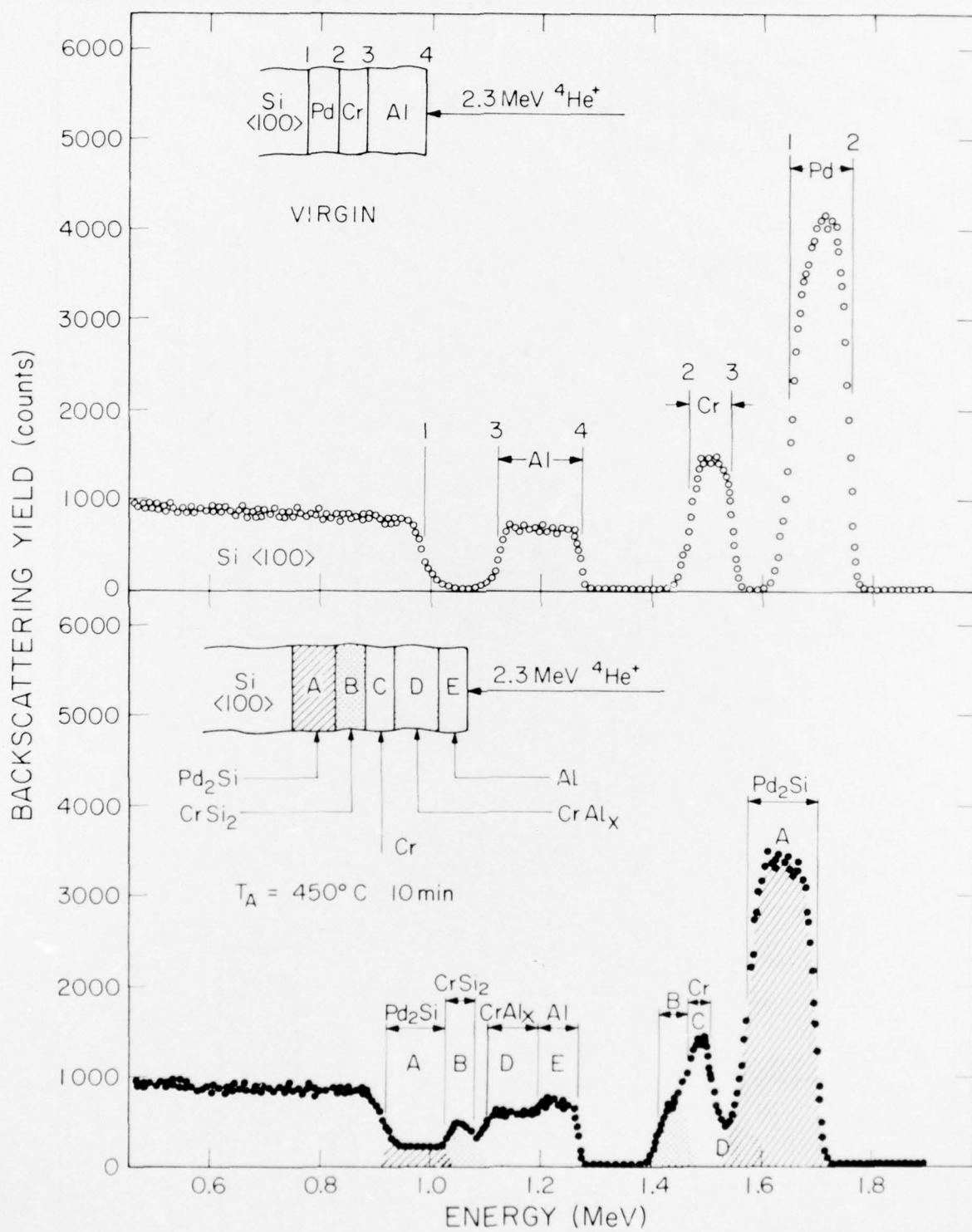
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